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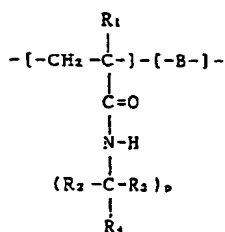
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(54) Improvements in and relating to polymeric resins and binders for antifouling paints

(57) The invention relates to hydrolysable polymeric resins of the general formula (2)



(2)

in which

R₁ = H, CH₃

R₂ = H, C₁-C₄-alkyl groups

R₃ = H, C₁-C₄-alkyl groups

p = 0 - 4

R₄ = (CH₂)_n (Y)_m (CH₂)_o N⁺R₅R₆R₇ X⁻ wherein

n = 0 - 6

m = 0, 1

Y = substituted phenyl rings of the general formula C₆H₂R₈R₉ wherein R₈, R₉ = H, CH₃, Br, Cl, NO₂, CN

o = 0 - 2

R₅, R₆, R₇ = H, linear or branched C₁-C₁₈-alkyl groups, substituted benzyl groups of the type -CH₂-C₆H₄R₁₀ wherein R₁₀ = H, Cl, Br, I, NO₂, CN, CH₃

X = Br, Cl, I

or

= (CH₂)_qCOOR₁₁ wherein

R₁₁ = H, C₁-C₆-alkyl groups, unsubstituted or monosubstituted benzyl or phenyl groups with H, Cl, Br, I, NO₂, CN, CH₃ as substituents

q = 0 - 2

B = constituent of the previously ethylenically unsaturated monomer with a percentage of ≥ 80% by weight, based on the total polymer,

which, as a result of hydrolytic cleavage on contact with water - especially with sea-water - is suitable as a slowly hydrolysing binder system for antifouling paints.

GB 2 273 934 A

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Improvements in and relating to polymeric resins and
binders for antifouling paints

The present invention relates to tin-free, water-soluble, slowly hydrolysable, polymeric binder systems
5 which - optionally in combination with biocides - can be used for protecting underwater surfaces from fouling by marine organisms.

Under suitable conditions, surfaces that come into contact with sea-water, such as, for example, boats,
10 ships, drilling platforms, nets or underwater pipelines, very quickly become covered with marine organisms, such as, for example, algae, seaweed, shells, tube-worms, fungi, etc..

In many cases, fouling of underwater surfaces by
15 such organisms leads to increased maintenance costs, and in the case of ships - owing to the increased frictional resistance in the water when the hull is fouled - to a marked reduction in speed or to a corresponding increase in fuel consumption.

20 Therefore, in order to prevent the surfaces from becoming fouled, the surface is in many cases protected by the application of a paint system containing suitable antifouling substances.

The antifouling substances are released from the
25 paint system through contact with sea-water and are thus able to develop their activity against marine organisms.

In order to achieve protection that is as long-lasting as possible against the possible surface colonising organisms, continuous release of the antifouling substance from the paint system in metered amounts is
5 sought.

In general, those paint systems - which are frequently also called antifouling systems or antifouling compositions - consist of a biocidal or non-biocidal polymeric binder, co-biocides and pigments.

10 Poly(meth)acrylates, polyesters, epoxy compounds, chlorine rubber, resins or other, film-forming systems are often used as polymeric binders.

The most successful antifouling paints in recent years have been so-called self-polishing paints, which
15 use binder systems in which the side groups of a linear polymer unit are split off in a first step by reaction with sea-water, the polymer framework that remains becoming water-soluble or water-dispersible as a result.

In a second step, the water-soluble portion of the
20 whole polymer is washed out of or eroded from the paint surface by the movement of the ship or of the surrounding water, a fresh surface which can again enter into a reaction with sea-water being provided at the same time. Such paint systems are described, for example, in
25 GB 1 124 297 and GB 1 457 590.

The advantage of those paint systems lies in the controlled rate of release of the incorporated biocides,

with the simultaneous formation of new, smooth surfaces.

The only binder systems having the above-mentioned properties which are relatively significant commercially are copolymers of triorganotin esters - especially tri-
5 n-butyltin esters - of olefinically unsaturated carboxylic acids. In many cases, substituted (meth)acrylic acids are used as unsaturated carboxylic acids.

In addition to the biocidal activity of the organotin group against marine organisms, those organotin-
10 containing binder systems are distinguished especially by the above-mentioned controllable hydrolysability in sea-water.

The fact that the underwater surfaces are as a result free from fouling owing to controllable rates of
15 release of the biocides and pigments used, and the simultaneous continuous polishing of the surfaces by the splitting off of the water-soluble portions of the polymer framework, are an important economic advantage of those systems.

20 The use of organotin-based antifouling systems especially in the yachting field, where such a powerful biocidal activity as that exhibited by the tri-n-butyltin compounds is unnecessary, has recently been the subject of lively discussion, and some countries have already
25 considerably restricted or even forbidden the use of organotin-based systems in the yachting field.

There is therefore a corresponding need in that

field for alternative paint systems that dissolve slowly in water.

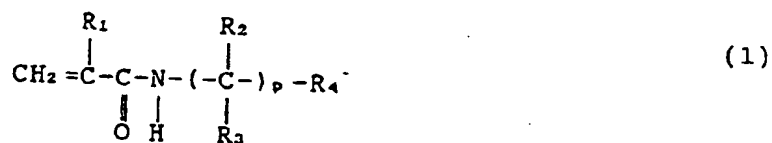
Various groups which likewise contain radicals that are hydrolysable in sea-water are mentioned in the literature as potential substitutes for the triorganotin compounds. However, they have not as yet become widely used commercially.

For example, WO 84/02915 mentions a number of possible groups which are said to form readily hydrolysable ester bonds with polymers containing carboxylic acid. EP-A-0 131 626, EP-A-0 201 279, EP-A-0 204 444, EP-A-0 204 456, EP-A-0 232 006, EP-A-0 289 481 and EP-A-0 343 897 also describe water-soluble polymer systems, some of which are self-polishing or erodable in contact with water.

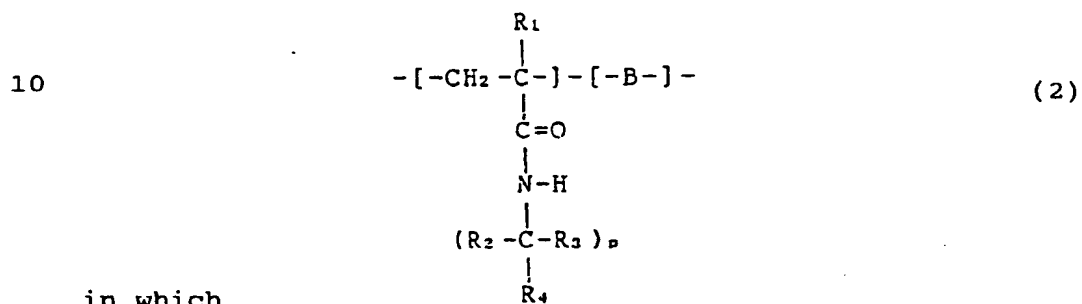
In a number of patent applications and patents (inter alia EP-A-0 113 038, EP-A-0 161 881, EP-A-0 250 325, EP-A-0 256 312, EP-A-0 419 654, EP-A-0 428 970, EP-A-0 464 957), processes for the preparation of quaternisation products of tertiary aminoalkylamides of acrylic and methacrylic acids, or the use of the polymeric, tertiary or quaternary aminoalkylamides as dispersing, flocculating or water-purifying agents or as adsorbent material for the liberation of water-soluble organic compounds, are described. The use of cyclic tertiary amides or imides as non-reactive components of anti-fouling binder systems is mentioned in EP-A-0 289 481.

The present invention describes a novel binder system suitable for use in water-soluble, slowly hydrolysable antifouling systems.

By copolymerisation of a monomeric unit of the
5 general formula (1)



with a suitable comonomer, it is possible to prepare the hydrolysable polymeric resins according to the invention of the general formula (2)



in which

R₁ is H or CH₃

R₂ is selected from H and C₁-C₄-alkyl groups

R₃ is selected from H and C₁-C₄-alkyl groups

15 p is from 0 - 4

R₄ is either (CH₂)_n (Y)_m (CH₂)_o N⁺R₅R₆R₇ X⁻ wherein

n is from 0 - 6

m is 0 or 1

Y is selected from substituted phenyl rings of the general formula $C_6H_2R_8R_9$ wherein R_8 , R_9 may be the same or different and each is selected from H, CH_3 , Br, Cl, NO_2 , CN

o is from 0 - 2

R_5 , R_6 , R_7 , which may be the same or different, are each selected from H, linear or branched C_1 - C_{18} -alkyl groups, and substituted benzyl groups of the type $-CH_2-C_6H_4R_{10}$ wherein $R_{10} = H$, Cl, Br, I, NO_2 , CN, CH_3

X is selected from Br, Cl, I

or

$(CH_2)_qCOOR_{11}$ wherein

R_{11} is selected from H, C_1 - C_6 -alkyl groups, and unsubstituted and monosubstituted benzyl and phenyl groups with one or more substituents selected from H, Cl, Br, I, NO_2 , CN and CH_3

q is from 0 - 2

and B is a constituent unit derived from a previously ethylenically unsaturated monomer, said unit being present in a percentage of $\geq 80\%$ by weight, based on the total polymer.

The invention provides polymeric resins of general

formula (2).

The invention provides also hydrolysable prepolymeric resins of the general formula (2) in which R_1 is CH_3 , R_2 and R_3 are each H and in which in R_4 the radicals R_5 and R_6 are each CH_3 and R_7 is a benzyl radical, with $n = 2$, $m = 0$, $o = 0$ and $p = 1$.

The invention further provides a polymeric binder system for an antifouling paint for protecting maritime surfaces, which system consists essentially of

- 10 a) a polymeric resin of the general formula (2) and, optionally,
- b) co-biocides and, optionally,
- c) customary auxiliaries, additives, pigments, plasticisers, levelling agents.

15 Moreover, the invention provides an antifouling paint comprising a hydrolysable polymeric resin which is the copolymerisation product of

(i) a compound of the formula



in which the group R is a group comprising a

quaternary ammonium or an ester group and the group R^1 is H or CH_3 ; and

(ii) an ethylenically unsaturated monomer, the proportion by weight in the copolymerisation product constituted by units derived from the ethylenically unsaturated monomer being not less than 80% by weight based on the total weight of the copolymerisation product. The group R is preferably a hydrocarbyl moiety to which a quaternary ammonium group is attached, the hydrocarbyl group optionally comprising one or more further substituents. The hydrocarbyl moiety may be an alkylene chain having up to nine carbon atoms in the chain, that may optionally be substituted by up to two C_1 - C_4 -alkyl groups. The hydrocarbyl group may be an alkylene chain having up to nine carbon atoms in the chain, which may be interrupted by, or have at a terminal position, a phenyl group which may optionally have one or more substituents selected from the group consisting of CH_3 , Br, Cl, NO_2 and CN. The group R may be an alkylene chain having a terminal carboxylic ester group, the alkylene chain having up to three carbon atoms in the chain and optionally being substituted by one or more C_1 - C_4 -alkyl groups.

The comonomers B used concomitantly according to the invention are ethylenically unsaturated monomers, such as, for example, acrylates or methacrylates, styrenes, acrylonitriles or vinyl compounds, but preferably a

monomeric acrylate or methacrylate compound, such as, for example, methacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, 5 propyl methacrylate, butyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, acrylamide.

In order to increase the water solubility and hydrolysability of the binder system as a whole, up to 10 % of the total amount of comonomer B may be replaced by 10 acrylic acid or alkylacrylic acid wherein alkyl represents a branched or unbranched C_1-C_8 group, or by corresponding alkyl acrylates with hydroxy groups.

The binder system according to the invention may be prepared by radical or ionic copolymerisation of the 15 corresponding amide compound with the comonomers.

In dependence upon the solubility properties of the starting monomers, there may be used as radical initiator, for example, benzoyl peroxide, azoisobutyronitrile, ammonium persulphate, 2,2-azo-bis-(2-amidinopropane) 20 dihydrochloride (concentration employed: 0.01 - 2 % by weight of the amount of monomer used) in a suitable solvent, such as, for example, toluene, xylene, cyclohexane, aliphatic hydrocarbons, such as, for example, hexane or heptane, butanol, methyl ethyl ketone, methyl 25 isobutyl ketone, ethyl acetate, butyl acetate, gasoline, water, dimethylformamide, dimethyl sulphoxide, ethers (e.g. ethylene glycol dimethyl ether, diethylene glycol

dimethyl ether), or mixtures of those solvents with one another (e.g. butanol/Solvesso 100 1:1).

For the purpose of copolymerisation, the starting materials and the initiator are heated in a suitable solvent under nitrogen or are added dropwise to the heated solvent.

In dependence upon the composition by percentage of the starting mixture, the reaction time, the rate of addition and the amount of initiator - and optionally, also by the addition of suitable inhibitors, such as, for example, mercaptans - it is possible to synthesise polymeric binder systems having different compositions and different molecular weights in the range of approximately from 50,000 to 150,000.

In the following, Examples 4 to 12 illustrate the invention. Examples 1 to 3 are Comparative Examples.

Examples

Example 1

300.3 g of methyl methacrylate (MMA), 255.5 g of dimethylaminopropyl-methacrylamide (DMAPMA) and 536.1 g of xylene are mixed together and de-aerated with nitrogen. Then 8.9 g of azoisobutyronitrile (AIBN) are added and the solution is copolymerised for 4 hours at 80°C in a nitrogen atmosphere, with stirring. A 50 % solution having a viscosity of 0.97 Pa·s is formed.

Example 2

150.1 g of methyl methacrylate (MMA), 213.3 g of butyl
methacrylate (BMA), 255.5 g of dimethylaminopropyl-meth-
acrylamide (DMAPMA) and 536.1 g of xylene are mixed
5 together under nitrogen. After the addition of 8.9 g of
azoisobutyronitrile (AIBN), the solution is heated to
80°C and copolymerised for 4 hours. A 50 % solution
having a viscosity of 1.01 Pa·s is formed.

Example 3

10 150.1 g of methyl methacrylate (MMA), 156.2 g of styrene
(STY), 255.5 g of dimethylaminopropyl-methacrylamide
(DMAPMA), 8.9 g of azoisobutyronitrile (AIBN) and 536.1 g
of xylene are mixed together and de-aerated with
nitrogen. The mixture is copolymerised for 4 hours at
15 80°C in a stream of nitrogen, with stirring. A 50 %
solution having a viscosity of 0.99 Pa·s is formed.

Example 4

Within a period of one hour, 126.6 g of benzyl chloride
are slowly added dropwise, with stirring, to a solution,
20 which is heated to 70°C, of 170 g of dimethylamino-
propyl-methacrylamide (DMAPMA) and 296.6 g of butanol.
The solution is stirred for a further hour at 70°C and
then cooled.

Example 5

Within a period of one hour, 141.9 g of methyl iodide are slowly added dropwise, with stirring, to a solution, which is heated to 70°C, of 170 g of dimethylamino-
5 propyl-methacrylamide (DMPMA) and 296.6 g of butanol. The solution is stirred for a further hour at 70°C and then cooled.

Example 6

80 g of a 50 % solution of the quaternary ammonium
10 compound (Example 4) in butanol are mixed together with 360 g of MMA, 9 g of dibenzoyl peroxide and a mixture of 260 g of butanol and 300 g of Solvesso 100, and the mixture is de-aerated with nitrogen. The mixture is copolymerised for 4 - 5 hours at 80°C in a stream of
15 nitrogen, with stirring. A 40 % solution having a viscosity of 9.7 Pa.s and a quaternary active ingredient content (percentage of the NR_4^+ group in the total polymer) of 10 % is formed.

Example 7

20 80 g of a 50 % solution of the quaternary ammonium compound (Example 5) in butanol are mixed together with 360 g of MMA, 9 g of dibenzoyl peroxide and a mixture of 260 g of butanol and 300 g of Solvesso 100, and the mixture is de-aerated with nitrogen. The mixture is
25 copolymerised for 4 - 5 hours at 80°C in a stream of

nitrogen, with stirring. A 40 % solution having a viscosity of 9.7 Pa·s and a quaternary active ingredient content (percentage of the NR_4^+ group in the total polymer) of 10 % is formed.

5 Example 8

80 g of the quaternary ammonium compound (50 % solution in butanol) of Example 4 are mixed together with 288 g of MMA, 72 g of butyl methacrylate, 8.6 g of dibenzoyl peroxide and a mixture of 260 g of butanol and 300 g of Solvesso 100. The mixture is copolymerised for 4 - 5 hours at 80°C in a stream of nitrogen, with stirring. A 40 % solution having a viscosity of 8 Pa·s and an active ingredient content of 10 % is formed.

Example 9

15 80 g of the quaternary ammonium compound (50 % solution in butanol) of Example 5 are mixed together with 288 g of MMA, 72 g of butyl methacrylate, 8.6 g of dibenzoyl peroxide and a mixture of 260 g of butanol and 300 g of Solvesso 100. The mixture is copolymerised for 4 - 5 hours at 80°C in a stream of nitrogen, with stirring. A 40 % solution having a viscosity of 8 Pa·s and an active ingredient content of 10 % is formed.

Example 10

75.5 g of the quaternary ammonium compound (50 % solution

in butanol) of Example 4 are mixed together with 250 g of MMA, 52 g of styrene, 9.4 g of dibenzoyl peroxide and a mixture of 207.6 g of butanol and 283.2 g of Solvesso 100, and the mixture is de-aerated with 5 nitrogen. The mixture is copolymerised for 4 - 5 hours at 80°C in a stream of nitrogen, with stirring. A 40 % solution having a viscosity of 1.2 Pa.s and an active ingredient content of 10 % is formed.

Example 11

10 75.5 g of the quaternary ammonium compound (50 % solution in butanol) of Example 5 are mixed together with 250 g of MMA, 52 g of styrene, 9.4 g of dibenzoyl peroxide and a mixture of 207.6 g of butanol and 283.2 g of Solvesso 100, and the mixture is de-aerated with 15 nitrogen. The mixture is copolymerised for 4 - 5 hours at 80°C in a stream of nitrogen, with stirring. A 40 % solution having a viscosity of 1.2 Pa.s and an active ingredient content of 10 % is formed.

Example 12

20 3-acrylamido-3-methyl-butanoic acid was prepared analogously to the method described by D.I. Hoke and R.D. Robins (J. Polym. Sci., 1972, 10, 3311-3315):

25.7 g of 3-acrylamido-3-methyl-butanoic acid and 16.2 g of benzyl alcohol are dissolved in 18 g of xylene and

90 g of diethylene glycol dimethyl ether (diglyme).

After the addition of 0.3 g of hydroquinone, 0.6 g of MBTO (mono-n-butyl tin oxide) and 0.5 ml of concentrated sulphuric acid as esterification catalysts, the water that forms as a result of the esterification is removed continuously for a period of 3 hours in vacuo at 80°C using a water separator. When the esterification is complete, 30 g of MMA and 1.5 g of AIBN are added and then the mixture is copolymerised for 4 hours at 80°C in a nitrogen atmosphere. A 40 % solution having a viscosity of 0.145 Pa·s is formed.

In order to determine the rates of hydrolysis of the binder systems according to the invention in alkaline medium, the changes in conductivity or pH with time were measured. Direct measurement in sea-water (pH: 8.1 - 8.3) was not possible for reasons concerning techniques of measurement (high intrinsic conductivity owing to the salt content).

The measurements were carried out as follows:

In a three-necked flask - equipped with a stirrer, a pH electrode (supplied by WTW, type E50-1.5) and a conductivity electrode (supplied by WTW, type LTA 1, cell constant 0.996) - 300 ml of bidistilled and degassed water were adjusted to a pH of 12 by the addition of NaOH pellets. The temperature of the whole system was kept constant at $25 \pm 0.1^\circ\text{C}$ (Haake thermostat GH-D8). The

measuring instruments used were a pH meter (supplied by
WTW, type pH 192) or a conductivity-measuring device
(supplied by WTW, type LF 530), which were connected to a
four-channel recorder (supplied by Linseis, type 2046,
5 modules G 14.186 and G 7406).

The binder system in solution was applied to glass
beads having a diameter of 3 mm and the solvent was
removed with the aid of a vacuum pump. The originally
weighted-in quantity of the polymeric binder system was
10 so selected that an approximately 50 % excess of sodium
hydroxide solution still remained after the reaction was
complete.

In order to determine the rates of hydrolysis, the
changes in conductivity or pH with time were then
15 measured and recorded via the recorder. The measurement
period was 24 hours.

The following Table clearly shows that the binder
system according to the invention hydrolyses slowly in
alkaline medium under the chosen conditions.

Table 1: Hydrolysis of binder systems

5	Binder system	Percentage of potential leaving groups hydrolysed within a period of 24 hours
	TBTM (monomer)	76.8
10	Standard copolymer (TBTM/MMA 1:2)	29.5
15	Polymer based on Example 4 (Ex.6)	14.9

TBTM is tri-n-butyl tin methacrylate.

For the preparation of the antifouling paint systems, the polymeric binder system according to the invention is mixed with pigments and, optionally, with
20 biocides in a suitable solvent.

The pigments are preferably pigments that are not readily soluble in water, such as, for example, copper oxide, copper thiocyanate, zinc oxide or zinc bis(dimethyldithiocarbamate), having additionally
25 biocidal properties, or non-biocidal, insoluble pigments, such as titanium dioxide or iron oxide.

The water-insoluble pigments used delay the hydrolytic dispersion of the antifouling paint system on account of their properties.

30 The concentrations of insoluble pigments used may be up to 40 % by weight of the total amount of pigment - but is preferably less than 20 % by weight.

The ratio of the polymeric binder to the total pigment concentration is to be such that the pigment

concentration by volume is over 25 % in the dry film - preferably, the pigment concentration by volume is from 35 to 50 %.

According to the invention, the following compounds
5 may be used inter alia as co-biocides in an amount of the order of from 2 to 25 % by weight, preferably from 2 to 12 % by weight:

dichlorophenyl-dimethylurea, 2-methylthio-tert.-butyl-
amino-6-cyclopropylamino-s-triazine, zinc pyrithione,
10 2-(thiocyanomethyl)benzothiazole, 4,5-dichloro-2-N-octyl-
4-isothiazolin-3-one, 2,4,5,6-tetrachlorophthalonitrile,
dichlofluanid.

Suitable solvents for those antifouling paints are,
for example, aliphatic and aromatic hydrocarbons, such
15 as, for example, toluene, xylene, heptane, and also
alcohols, such as butanol, ketones, such as methyl
isobutyl ketone, or esters, such as ethyl or butyl
acetate, petroleum hydrocarbon fractions, such as, for
example, ligroin, gasoline, or also water, dimethylfor-
20 mamide, or mixtures of the mentioned solvents with one
another (e.g. butanol/Solvesso 100 1:1).

The paint systems may also contain a plasticiser,
for example tritolyl phosphate, diisooctyl phthalate,
tributyl phosphate, polyvinyl methyl ether or a substi-
25 tuted sulphonamide, such as, for example, N-ethyl-p-
toluenesulphonamide, as well as other auxiliaries,
dispersing agents, anti-settling agents, fillers,

accelerators, inhibitors, colouring agents or siccatives, such as, for example, talc, Bentone, cobalt naphthenate, blue pigments.

The antifouling paint films are applied to the
5 surface to be protected by means of the methods customarily employed, such as, for example, immersion, coating, spraying or sprinkling.

Antifouling paint 1

73.2 g of the copolymer of Example 1 (40 % solution in
10 xylene), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (gelling agent based on montmorillonite earth, Titangesellschaft, 6 % solution in xylene) and 10 g of xylene are ground intensively for one hour.

Antifouling paint 2

15 73.2 g of the copolymer of Example 2 (40 % solution in xylene), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (6 % solution in xylene) and 10 g of xylene are ground intensively for one hour.

Antifouling paint 3

20 73.2 g of the copolymer of Example 3 (40 % solution in xylene), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (6 % solution in xylene) and 10 g of xylene are ground intensively for one hour.

Antifouling paint 4

73.2 g of the copolymer of Example 2 (40 % solution in butanol/Solvesso 100 1:1), 20 g of titanium dioxide RN 57 and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 5

73.2 g of the quaternary ammonium compound of Example 6 (40 % solution in butanol/Solvesso 100 1:1), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (gelling agent based on montmorillonite earth, Titan-gesellschaft) (6 % solution in xylene) and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 6

73.2 g of the quaternary ammonium compound of Example 7 (40 % solution in butanol/Solvesso 100 1:1), 20 g of titanium dioxide RN 57 (Bayer) and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 7

73.2 g of the quaternary ammonium compound of Example 8 (40 % solution in butanol/Solvesso 100 1:1), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (6 % solution in xylene) and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 8

73.2 g of the copolymer of Example 9 (40 % solution in butanol/Solvesso 100 1:1), 20 g of titanium dioxide RN 57 and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 9

73.2 g of the quaternary ammonium compound of Example 10 (40 % solution in butanol/Solvesso 100 1:1), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone (6 % solution in xylene) and 10 g of butanol/Solvesso 100 1:1 are ground intensively for one hour.

Antifouling paint 10

73.2 g of the copolymer of Example 12 (40 % solution in xylene), 5 g of copper(I) oxide, 13 g of zinc oxide, 11.1 g of Bentone 38 (6 % solution in xylene) and 10 g of xylene are ground intensively for one hour.

When the substituent R_4 is a quaternary ammonium compound of the type $N^+R_5R_6R_7X^-$, the binder system according to the invention exhibits biocidal activity against marine organisms. The substituents R_5 , R_6 , R_7 here correspond to branched or unbranched C_1 - C_{18} -alkyl groups or substituted benzyl groups of the type $-CH_2-C_6H_4R_{10}$ wherein $R_{10} = H, Cl, Br, I, NO_2, CN, CH_3$.

The biocidal effect of the binder system according

to the invention with the substituents $-N^+R_5R_6R_7X^-$ can be strengthened or broadened by the use of poorly water-soluble pigments, such as copper oxide, copper thiocyanate or zinc thiocarbamates, or additionally by other biocides, such as, for example, 2,4,5,6-tetrachloroisophthalonitrile, 2-methylthio-4-tert.-butylamino-6-cyclopropylamino-s-triazine, 2-thiocyanomethyl-thiobenzothiazole, 3-(3,4-dichlorophenyl)-1,1-dimethylurea, 3-iodo-2-propynyl butylcarbamate, dibromosuccinates, dichlofluanid, diphenylamine, isothiazolones, manganese ethylenebisdithiocarbamate, organometal compounds, tetramethylthiuram disulphide, zinc bis(dimethyldithiocarbamate), zinc pyrithione.

The activity of the binder systems according to the invention against marine organisms was determined by means of ageing tests both in the Mediterranean and in the North Sea.

For that purpose, polyvinyl chloride test plates (10 x 15 x 0.4 cm) were provided with antifouling paints.

After degreasing, the PVC plates were painted with two coats of the antifouling composition and dried for 48 hours. The thickness of the dry film was from 80 to 120 μm .

The PVC plates were then clamped in a plastics frame and aged for a period of 12 months approximately 0.3 - 0.5 m beneath the water surface. Untreated PVC plates were used as reference sample.

The following Table clearly shows that the binder systems according to the invention, in which R_4 is a quaternary ammonium compound of the type $-N^+R_5R_6R_7X^-$, exhibit biocidal activity against animal and vegetable fouling during the observation period.

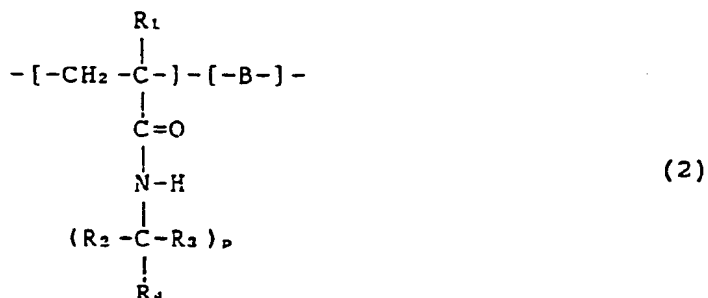
The test plates without the compounds according to the invention exhibited considerable fouling by algae, Balanidae and shells.

Table 2

		3 months	6 months	12 months
15	Antifouling paint 5	0	1	2
	Antifouling paint 6	0	3	5
20	Antifouling paint 7	0	2	3
	Antifouling paint 8	0	2	5
	Antifouling paint 9	0	1	3
25	Comparative examples			
	Untreated PVC plate	10	10	10
30	Antifouling paint 1	0	4	8
35	0 = no fouling 5 = 50 % fouling 10 = complete fouling			

Claims

1. A hydrolysable polymeric resin of the general formula



5 in which

R_1 is H or CH_3

R_2 is selected from H and C_1 - C_4 -alkyl groups

R_3 is selected from H and C_1 - C_4 -alkyl groups

p is from 0 - 4

10 R_4 is either $(CH_2)_n (Y)_m (CH_2)_o N^+R_5R_6R_7 X^-$ wherein

n is from 0 - 6

m is 0 or 1

Y is selected from substituted phenyl rings of the general formula $C_6H_2R_8R_9$ wherein R_8, R_9

15 may be the same or different and each is selected from H, CH_3 , Br, Cl, NO_2 , CN

o is from 0 - 2

R_5, R_6, R_7 , which may be the same or different, are each selected from H, linear or branched

20 C_1 - C_{18} -alkyl groups, and substituted benzyl

groups of the type $-\text{CH}_2-\text{C}_6\text{H}_4\text{R}_{10}$ wherein

$\text{R}_{10} = \text{H}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{CN}, \text{CH}_3$

X is selected from Br, Cl, I

or

5 $(\text{CH}_2)_q\text{COOR}_{11}$ wherein

R_{11} is selected from H, $\text{C}_1\text{-C}_6$ -alkyl groups, and unsubstituted and monosubstituted benzyl and phenyl groups with one or more substituents selected from H, Cl, Br, I,

10 NO_2, CN and CH_3

q is from 0 - 2

and B is a constituent unit derived from a previously ethylenically unsaturated monomer, said unit being present in a percentage of $\geq 80\%$ by weight, based on the total polymer.

15

2. A hydrolysable prepolymeric resin of the general formula (2) in which R_1 is CH_3 , R_2 and R_3 are each H and in which in R_4 the radicals R_5 and R_6 are each CH_3 and R_7 is a benzyl radical, with $n = 2$, $p = 1$, $m = 0$, $o = 0$.

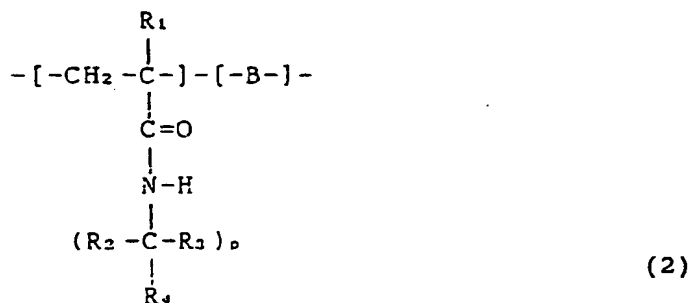
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3. A hydrolysable polymeric resin according to claim 1, in which from 2 to 5 % by weight of the constituent units B of the general formula (2) are units derived from acrylic acid.

4. A polymeric binder system for an antifouling paint for protecting maritime surfaces, which system consists essentially of

25

a) a polymeric resin of the general formula (2)



in which

R_1 is H or CH_3

R_2 is selected from H and C_1 - C_4 -alkyl groups

5 R_3 is selected from H and C_1 - C_4 -alkyl groups

p is from 0 - 4

R_4 is either $(CH_2)_n (Y)_m (CH_2)_o N^+R_5R_6R_7 X^-$ wherein

n is from 0 - 6

m is 0 or 1

10 Y is selected from substituted phenyl rings of the general formula $C_6H_2R_8R_9$ wherein R_8, R_9 may be the same or different and each is selected from H, CH_3 , Br, Cl, NO_2 , CN

o is from 0 - 2

15 R_5, R_6, R_7 , which may be the same or different, are each selected from H, linear or branched C_1 - C_{18} -alkyl groups, and substituted benzyl groups of the type $-CH_2-C_6H_4R_{10}$ wherein $R_{10} = H, Cl, Br, I, NO_2, CN, CH_3$

20 X is selected from Br, Cl, I

or

$(CH_2)_q COOR_{11}$ wherein

R_{11} is selected from H, C_1 - C_6 -alkyl groups, and unsubstituted and monosubstituted benzyl and phenyl groups with one or more substituents selected from H, Cl, Br, I, NO_2 , CN and CH_3

q is from 0 - 2

and B is a constituent unit derived from a previously ethylenically unsaturated monomer, said unit being present in a percentage of ≥ 80 % by weight, based on the total polymer, and, optionally,

- b) one or more co-biocides and, optionally,
- c) one or more substances selected from customary auxiliaries, additives, pigments, plasticisers, levelling agents.

5. A polymeric binder system according to claim 4, in which the polymeric resin according to a) is used in an amount of from 15 to 40 % by weight, based on the total system.

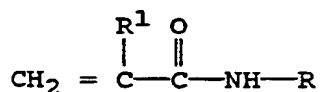
6. A polymeric binder systems according to claim 3 or claim 4, in which in there are used as co-biocides dichlorophenyl-dimethylurea, 2-methylthio-tert.-butyl-amino-6-cyclopropylamino-s-triazine, zinc pyrithione, 2-(thiocyanomethyl)benzothiazole, 4,5-dichloro-2-N-octyl-4-isothiazolin-3-one, 2,4,5,6-tetrachlorophthalonitrile,

dichlofluanid.

7. An antifouling paint comprising a hydrolysable polymeric resin which is the copolymerisation product of

(i) a compound of the formula

5



in which the group R is a group comprising a
10 quaternary ammonium or an ester group and the group R¹ is
H or CH₃; and

(ii) an ethylenically unsaturated monomer,
the proportion by weight in the copolymerisation
product constituted by units derived from the
15 ethylenically unsaturated monomer being not less than 80%
by weight based on the total weight of the
copolymerisation product.

8. A paint as claimed in claim 7, in which the
group R is a hydrocarbyl moiety to which a quaternary
20 ammonium group is attached, the hydrocarbyl group
optionally comprising one or more further substituents.

9. A paint as claimed in claim 8, in which the
hydrocarbyl moiety is an alkylene chain having up to
nine carbon atoms in the chain, that may optionally be

substituted by up to two C₁-C₄-alkyl groups.

10. A paint as claimed in claim 8 or claim 9, in which the hydrocarbyl moiety is an alkylene chain having up to nine carbon atoms in the chain which may be
5 interrupted by, or have at a terminal position, a phenyl group which may optionally have one or more substituents selected from the group consisting of CH₃, Br, Cl, NO₂ and CN.

11. A paint as claimed in claim 7, in which the
10 group R is an alkylene chain having a terminal carboxyl ester group, the alkylene chain having up to three carbon atoms in the chain and optionally being substituted by one or more C₁-C₄-alkyl groups.

12. An antifouling paint as claimed in any of claims
15 7 to 11, in which said resin comprises units of the general formula (2) as defined in claim 1.

13. An antifouling paint comprising a hydrolysable polymeric resin according to any of claims 1 to 3 or a polymeric binder system according to any one of claims 4
20 to 6.

14. An antifouling paint comprising a copolymer, said copolymer being substantially as described in any of Examples 6 to 12.

15. An antifouling paint substantially as described
25 herein as Antifouling paint 5, Antifouling paint 6, Antifouling paint 7, Antifouling paint 8, Antifouling paint 9 or Antifouling paint 10.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

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Application number
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Relevant Technical Fields

- (i) UK Cl (Ed.M) C3P - PFE, PDT, PDR C3V - VABG, VACA
 (ii) Int Cl (Ed.5) C08F, C09D

Search Examiner
 M J PRICE

Date of completion of Search
 28 FEBRUARY 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
 1-15

(ii) ONLINE DATABASES: WPI

Categories of documents

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.
 Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
 A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1359932	(LUBRIZOL) - see eg Claim 1	1 at least
X	GB 1097054	(BAYER) - see Experiment II	1 at least
X	GB 788079	(ICI) - see the claims and examples	1 at least
X	GB 769732	(CYANAMID) - see eg Examples 5 and 8	1 at least
X	US 4835234	(EXXON) - see eg the examples	1 at least
X	US 4649183	(MISSISSIPPI) - the whole documents eg column 5 lines 31-35	1 at least
X	US 4594365	(M & T) - see eg the examples	4 and 7 at least

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